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CYCLOHEXANE DEHYDROGENATION ON CLEAN Pd SURFACES STUDIED BY UV PHOTOEMISSION

by

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G. W. Rubloff, H. Lüth†, J. E. Demuth, and W. D. Grobman

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ABSTRACT

Ultraviolet photoemission studies show that cyclohexane is adsorbed without decomposition on clean polycrystalline Pd and single crystal Pd (111) surfaces at low temperature ($\leq$120 K), but at 300 K it dehydrogenates to leave chemisorbed benzene on the surface.

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Ultraviolet photoemission spectroscopy (UPS) has been applied with considerable success over the past few years to the study of surface reactions involving relatively small organic molecules.[1-7] We consider here the behavior of a somewhat larger molecule, cyclohexane (C_6H_{12}), on clean Pd surfaces. Our UPS studies show that C_6H_{12} dehydrogenates to yield chemisorbed benzene (C_6H_6) on clean Pd (111) and on polycrystalline Pd surfaces at 300 K.

Details of the experimental techniques have been described previously.[3] The clean polycrystalline Pd films were evaporated in ultrahigh vacuum (operating pressure $< 10^{-10}$ torr) and could be cooled to 120 K and electrically heated for annealing. The Pd (111) surface was prepared by orienting (to $\pm$ 1/4°), cutting, and mechanically polishing a (111) plane of a Pd single crystal. The surface was then cleaned in situ by ion bombardment, oxygen treatment, and annealing cycles. The Pd (111) surface could be cooled to ~80 K. Adsorbate gases of C_6H_{12} and C_6H_6 were obtained from the equilibrium vapor pressure over reagent grade liquids and monitored using a quadrupole mass spectrometer. The UPS measurements on the Pd surfaces were made using a differentially-pumped He resonance lamp (photon energies He I = 21.2 eV and He II = 40.8 eV) and a double-pass cylindrical mirror analyzer (at a resolution of ~ 0.35-0.4 eV) in conjunction with electron counting techniques. Gas phase spectra for C_6H_{12}, C_6H_{10}, C_6H_8, and C_6H_6 were obtained using a similar apparatus.

The UPS spectrum of the clean polycrystalline Pd surface at $h\nu$ = 40.8 eV is shown by the dotted line in Fig. 1a. Electron binding energies (BE) are referenced to an energy zero at the Fermi level (E_F). The Pd(4d) bands give a pronounced structure between ~ 5 eV BE and E_F. (The enhanced intensity for BE > 16 eV in Fig. 1 is Pd(4d) emission excited by the 21.2 eV He I radiation from the resonance lamp). The work function of the clean surface, obtained from the full width (not shown) of the spectral distribution, is ϕ = 5.6 eV. The spectrum of the clean surface is in general agreement with that measured by Küppers et. al.[8] on polycrystalline Pd, although it exhibits less pronounced d-band structure than that observed on single-crystal Pd surfaces.[9]

Exposing the surface, while at 120 K, to 20 L (1 L = langmuir = 10^{-6} torr-sec) of C_6H_{12} reduces the work function by $\Delta\phi$ = -0.5 eV and yields the spectrum shown by the dashed line in Fig. 1a. Emission from the Pd d-bands has been suppressed and new adsorbate-induced features are seen at ~ 3.7, 6.0, 8.3, 11.2, and 12.8 eV. In contrast, with the clean Pd surface held at 300 K, a 25 L exposure of C_6H_{12} reduces the work function by $\Delta\phi$ = -0.8 eV and shows new spectral features at ~ 3.9, 5.8, 8.5, 10.8, and 13.2 eV as seen in the solid curve in Fig. 1a. The exposures at 120 K (20 L) and 300 K (25 L) give comparable magnitudes for the adsorbate orbitals and d-band attenuation, suggesting that a similar adsorbate coverage is produced. Although there is a correspondence between peaks in the range 0-10 eV BE in the spectra for the 120 K and 300 K C_6H_{12} exposures, these spectra differ measurably in their peak positions and relative intensities between 10 and 14 eV BE. These differences lead us to conclude that different adsorbed molecular species are produced by cyclohexane exposure at 300 K as opposed to 120 K.

The differences between the spectra for the 120 K and 300 K C_6H_{12} exposures appear even more clearly in the "difference curves" (i.e. spectrum for adsorbate-covered surface minus spectrum for clean surface) shown in Fig. 1b. Again, although the peaks between ~ 3-9 eV BE are within 0.2-0.3 eV of each other in the two spectra, the two peaks between 10-14 eV differ measurably in position and in relative intensity: their separation is 1.6 eV (vs. 2.4 eV) in the 120 K (vs. 300 K) spectrum, and the stronger peak of the two lies at larger (vs. smaller) BE for the 120 K (vs. 300 K) spectrum.

In Fig. 2 we compare the difference spectra to gas phase spectra in order to identify the adsorbed species. The difference curve for the 20 L C_6H_{12} exposure at low temperature is reproduced in Fig. 2a for comparison with the gas phas UPS spectrum of C_6H_{12} as measured in our laboratory and shown in Fig. 2b. The gas phase ionization potentials are shown by the IP scale. Ionization potentials for the adsorbed molecule are given by $IP_{surf} = BE_{surf}$ (referenced to $E_F = 0$) + ϕ + $\Delta\phi$. By shifting the gas phase spectrum uniformly toward

smaller BE by ΔE_R = 2.0 eV, all the orbitals in the gas phase spectrum are brought into coincidence with those of the difference curve in Fig. 2a to within ~ ± 0.2 eV. This shift accounts for the effects of extramolecular relaxation and polarization associated with the altered environment of the molecule on the surface; often these effects can be approximately represented by a uniform shift of all those valence molecular orbitals not directly involved in forming the chemisorption bond.[10]

Because of the close correspondence between the spectra in Figs. 2a and 2b, we identify the adsorbed species resulting from C_6H_{12} exposure to the clean Pd surface at 120 K as adsorbed C_6H_{12} having no appreciable chemical interaction with the Pd surface. Measurements carried out at 120 K in a 1×10^{-7} torr C_6H_{12} ambient gave a spectrum essentially the same as that in Fig. 1a but with adsorbate orbitals more intense and lying at ~ 0.8 eV larger BE. We therefore associate the species represented in Fig. 2a with physisorbed C_6H_{12} ($\leq$ 1 monolayer) in contact with the Pd surface. The additional species formed in an ambient of C_6H_{12} is associated with a condensed C_6H_{12} overlayer having a smaller ΔE_R = 1.2 eV. The absence of significant chemical interaction between the first, physisorbed C_6H_{12} layer and the transition metal surface is consistent with previous results obtained for saturated hydrocarbons in Ni(111).[1,11,12]

The difference spectrum at $h\nu$ = 40.8 eV for the 25 L C_6H_{12} exposure at 300 K is reproduced in Fig. 2c. Also shown is the corresponding result for $h\nu$ = 21.2 eV (dot-dashed curve). In Fig. 2d we show the difference curve at $h\nu$ = 40.8 eV for a 20 L exposure of benzene (C_6H_6) to the clean Pd surface, which produces a larger work function change $\Delta\phi$ = -1.4 eV. The spectral structure observed for this C_6H_6 exposure is virutally identical to that obtained by the C_6H_{12} exposure at 300 K. The gas phase UPS spectrum of C_6H_6 at $h\nu$ = 40.8 eV is shown in Fig. 2e, shifted uniformly toward smaller BE in order to align it with the difference curves in Figs. 2c and 2d.

The close similarity between Figs. 2d and 2e shows that C_6H_6 adsorbs without decomposition on the polycrystalline Pd surface. The highest-lying π orbitals of C_6H_6 undergo a shift of ~ 0.7 eV toward larger BE relative to the other valence orbitals. This shift, depicted by the arrows in Figs. 2d and 2e, is associated with chemisorption of the molecule through these π orbitals, as found previously on Ni(111).[1] The relaxation/polarization shift here is ΔE_R = 1.9 eV.

C_6H_{12} exposure to the clean polycrystalline Pd surface at 300 K gives essentially the same spectrum (Fig. 2c) as that of chemisorbed C_6H_6 (fig. 2d). We therefore conclude that the C_6H_{12} is dehydrogenated to chemisorbed C_6H_6 on clean polycrystalline Pd at 300 K. This dehydrogenated species (at 25 L exposure) gives $\Delta\phi$ = -0.8 eV and ΔE_R = 1.3 eV. Because the C_6H_{12} does not decompose at low temperature, the dehydrogenation reaction must involve a thermal activation barrier.[1]

The 20 L C_6H_6 exposure produced larger (by ~2X) spectral changes (both d-band attenuation and adsorbate orbital intensities) than did the 25 L C_6H_{12} exposure at 300 K, suggesting that ~2X as much chemisorbed C_6H_6 is formed from this C_6H_6 exposure than from dehydrogenation associated with the C_6H_{12} exposure. We attribute the smaller $|\Delta\phi|$ observed in the latter case to the lower C_6H_6 coverage produced. The dehydrogenation of C_6H_{12} to C_6H_6 on Pd may leave chemisorbed atomic hydrogen on the surface as well, since hydrogen itself is known to chemisorb on Pd at 300 K (~21 kcal/mole binding energy).[13] Hydrogen adsorption on Pd produces only weak, fairly broad structures in the UPS spectrum,[3,9] so that no additional peaks are expected or observed for dehydrogenated C_6H_{12} (Fig. 2c) compared with chemisorbed C_6H_6 (Fig. 2d).

UPS measurements of C_6H_{12} on Pd(111) also reveal the dehydrogenation of C_6H_{12} to C_6H_6 at 300 K. Figure 3a shows the UPS difference curve (at $h\nu$ = 21.2 eV) for a 7 L C_6H_{12} exposure to the clean Pd(111) surface at ~80 K. More detailed structure is evident in the

d-band region and below for this single crystal surface than for the polycrystalline Pd surface. The work function continues to change with higher exposures, suggesting that the spectrum in Fig. 3a represents less than saturation coverage for C_6H_{12} adsorbed on the Pd(111) surface; above ~11 L, the spectrum of a multilayer condensed C_6H_{12} film appears and $\Delta\phi$ saturates.

At 300 K, larger C_6H_{12} exposures ($\geq$ 20 L) are required to significantly affect the UPS spectrum of Pd(111), indicating a much smaller effective sticking probability. The difference curve corresponding to a 40 L C_6H_{12} exposure at 300 K, shown in Fig. 3b, differs considerably (especially between 4 and 8 eV BE) from that for the 80 K C_6H_{12} exposure in Fig. 3a. The spectrum in Fig. 3b is virtually identical to that corresponding to a 2L C_6H_6 exposure to Pd(111) at 300 K shown in Fig. 3c. This demonstrates that C_6H_{12} dehydrogenates on Pd(111) at 300 K to leave chemisorbed C_6H_6 on the surface.

The question might also arise as to whether the dehydrogenated species formed from C_6H_{12} exposure at 300 K might be in fact a partially dehydrogenated species between C_6H_{12} and C_6H_6, in particular the stable molecules cyclohexene (C_6H_{10}) or 1,3 cyclohexadiene (C_6H_8). We have measured the gas phase UPS spectra of C_6H_{10} and C_6H_8 and find that our dehydrogenated phase cannot be attributed to these molecules. In particular, the positions of peaks in the gas phase spectra of C_6H_{10} and C_6H_8 are considerably different from those in the spectra of C_6H_{12} and C_6H_6, much more so than the differences between the C_6H_{12} and C_6H_6 gas phase spectra.[14] Thus we conclude that any partially dehydrogenated species rapidly converts to form C_6H_6, which is the stable reaction product in the dehydrogenation of C_6H_{12} on polycrystalline Pd and Pd(111) surfaces at 300 K. In contrast, UPS studies have shown that C_6H_{12} does not decompose on the clean Ni(111) surface at 300 K.[12]

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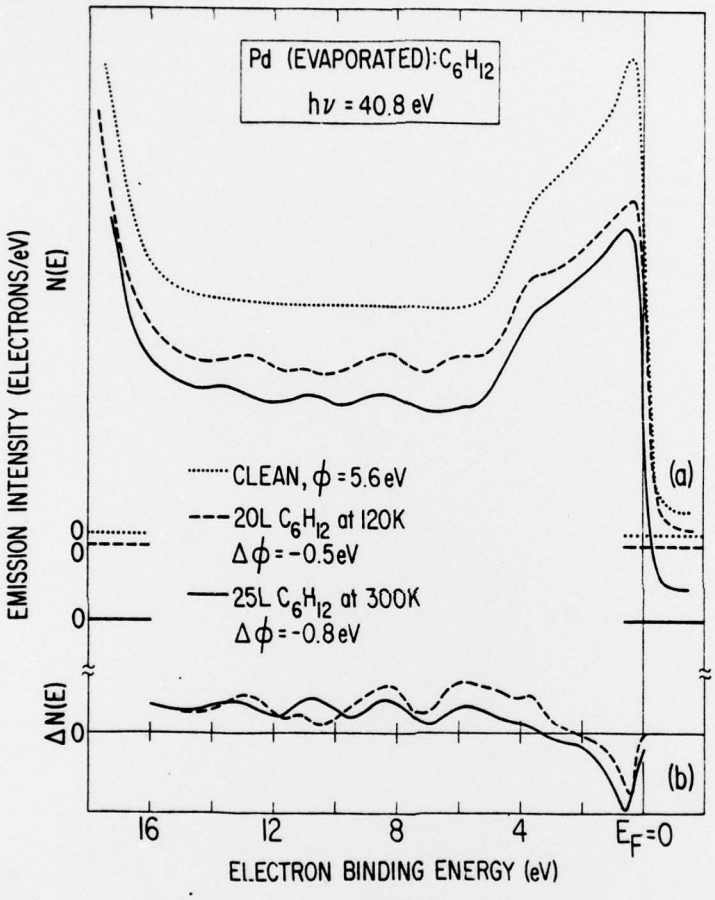

Fig. 1. (a) UPS spectra at $h\nu$ = 40.8 eV for the clean polycrystalline Pd surface (dotted curve) and for the same surface exposed to 20 L of C_6H_{12} at 120 K (dashed curve) and 25 L of C_6H_{12} at 300 K (solid curve). Spectra have been shifted vertically for clarity, as indicated by the position of zero marks.

(b) corresponding UPS difference curves for the 120 K (dashed) and 300 K (solid) C_6H_{12} exposures to the clean polycrystalline Pd surface.

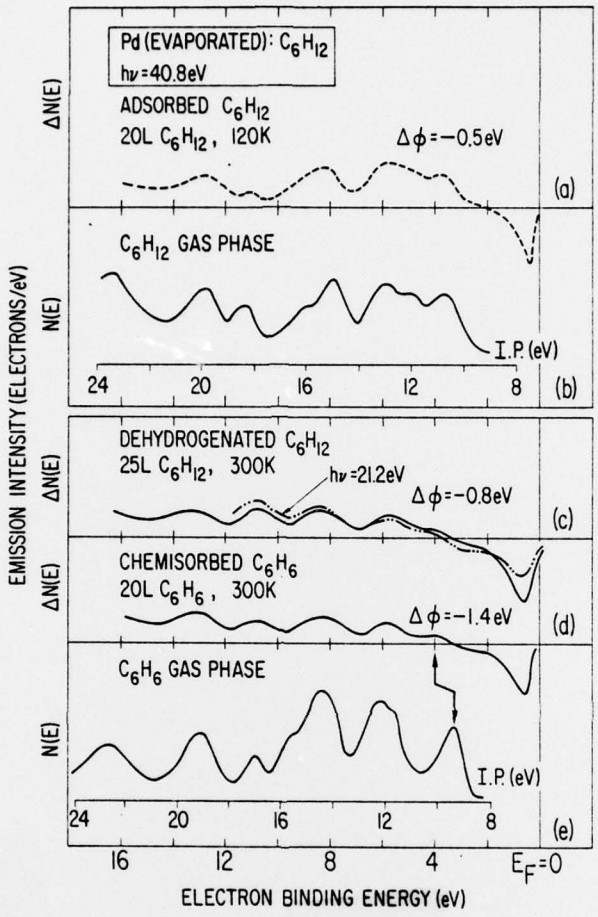

Fig. 2. UPS spectra at $h\nu$ = 40.8 eV:

(a) difference curve for 20 L C_6H_{12} exposure to polycrystalline Pd at 120 K;

(b) gas phase spectrum of C_6H_{12}, with gas phase ionization potentials (I. P. scale) shifted uniformly toward smaller binding energy to align with Fig. 2a;

(c) difference curve for 25 L C_6H_{12} exposure to polycrystalline Pd at 300 K, including also the corresponding difference curve for $h\nu$ = 21.2 eV (dot-dash curve);

(d) difference curve for a 20 L C_6H_6 exposure to polycrystalline Pd at 300 K;

(e) gas phase spectrum of C_6H_6, shifted toward smaller binding energy to align with Figs. 2c and 2d.

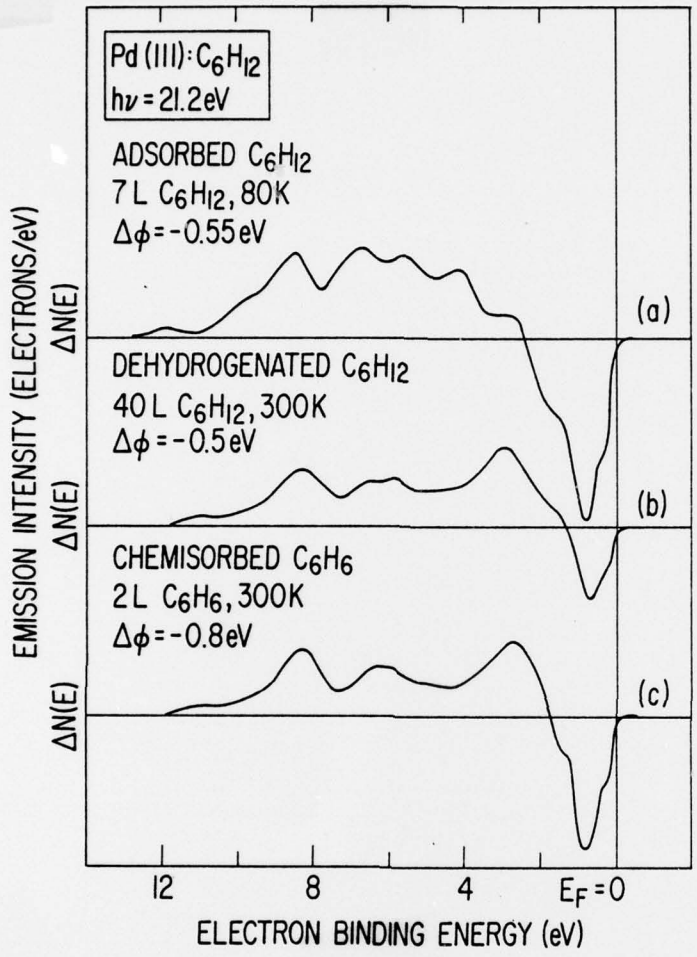

Fig. 3. UPS difference curves at $h\nu$ = 21.2 eV for exposures to the clean Pd(111) surface:

(a) 7 L C_6H_{12} at 80 K;

(b) 40 L C_6H_{12} at 300 K;

(c) 2 L C_6H_6 at 300 K.

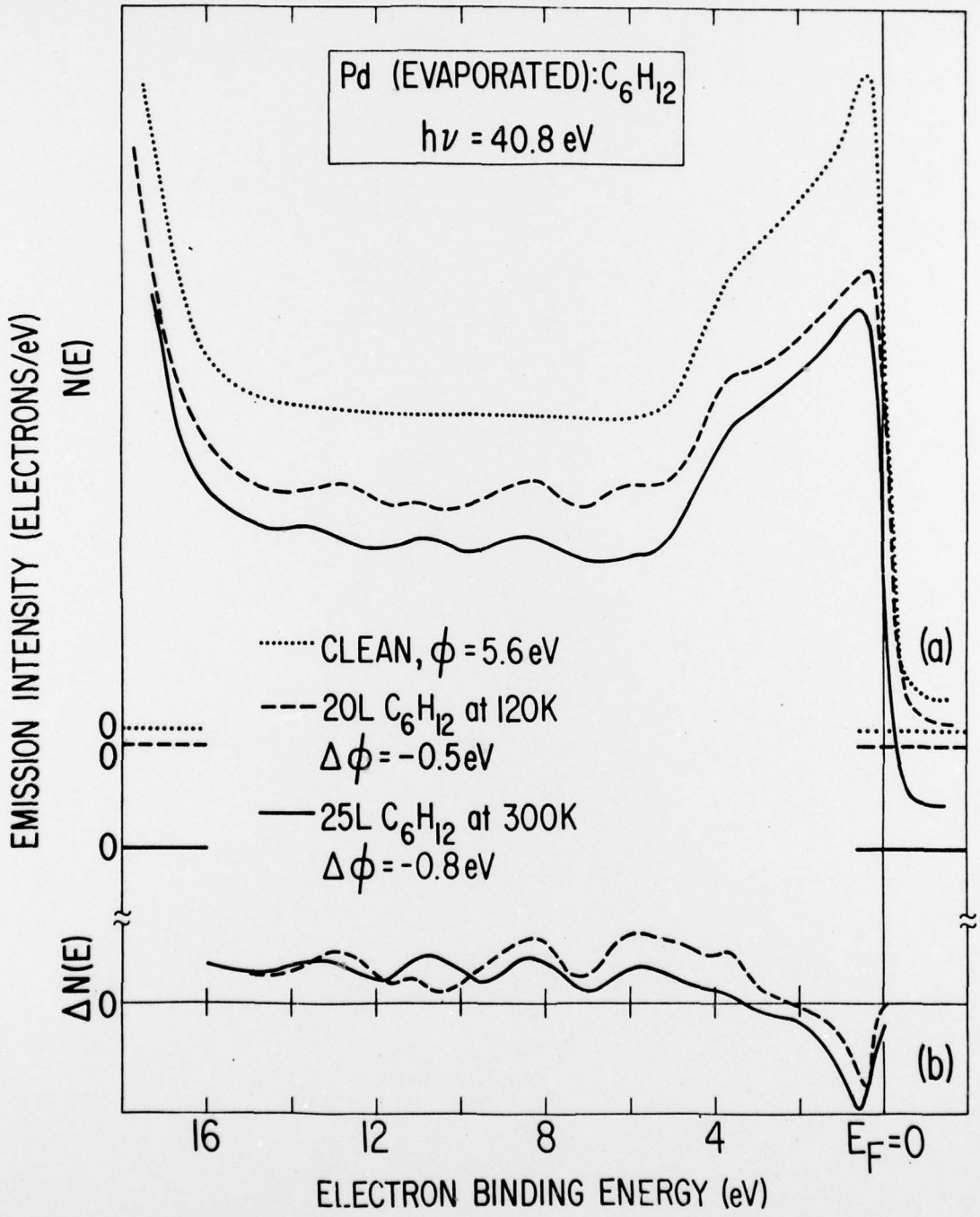
Pd (EVAPORATED):C6H12
hν = 40.8 eV
EMISSION INTENSITY (ELECTRONS/eV)
N(E)
CLEAN, φ = 5.6 eV
20L C6H12 at 120K
Δφ = -0.5 eV
25L C6H12 at 300K
Δφ = -0.8 eV
(a)
(b)
0
0
0
ΔN(E)
0
16
12
8
4
EF=0
ELECTRON BINDING ENERGY (eV)

Fig. 1.

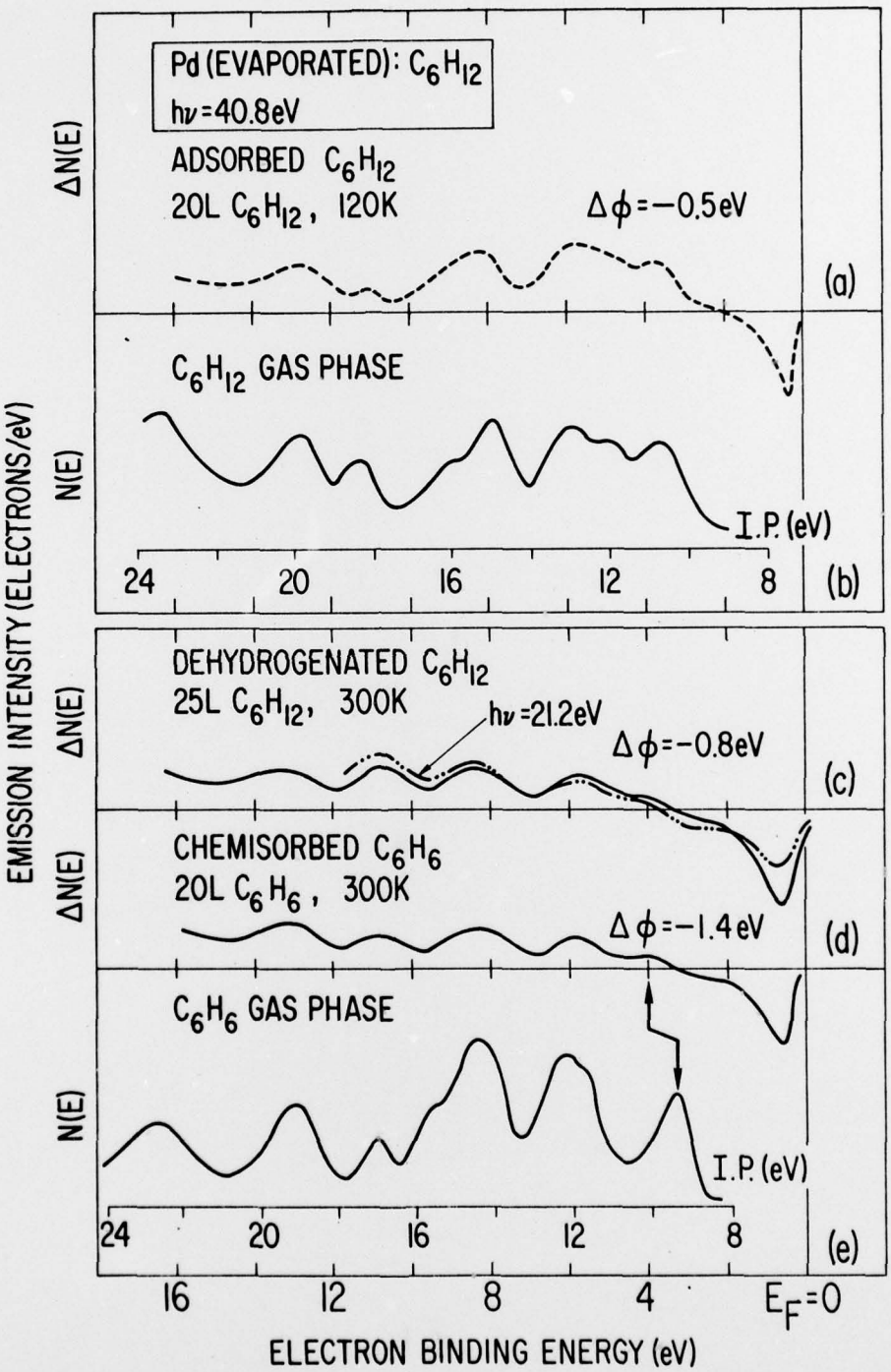
Pd (EVAPORATED): C_6H_{12}
$h\nu$ = 40.8eV
ADSORBED C_6H_{12}
20L C_6H_{12}, 120K
$\Delta\phi$ = −0.5eV
(a)
C_6H_{12} GAS PHASE
I.P. (eV)
24
20
16
12
8
(b)
DEHYDROGENATED C_6H_{12}
25L C_6H_{12}, 300K
$h\nu$ = 21.2eV
$\Delta\phi$ = −0.8eV
(c)
CHEMISORBED C_6H_6
20L C_6H_6, 300K
$\Delta\phi$ = −1.4eV
(d)
C_6H_6 GAS PHASE
I.P. (eV)
24
20
16
12
8
(e)
ΔN(E)
N(E)
EMISSION INTENSITY (ELECTRONS/eV)
16
12
8
4
E_F = 0
ELECTRON BINDING ENERGY (eV)

Fig. 2

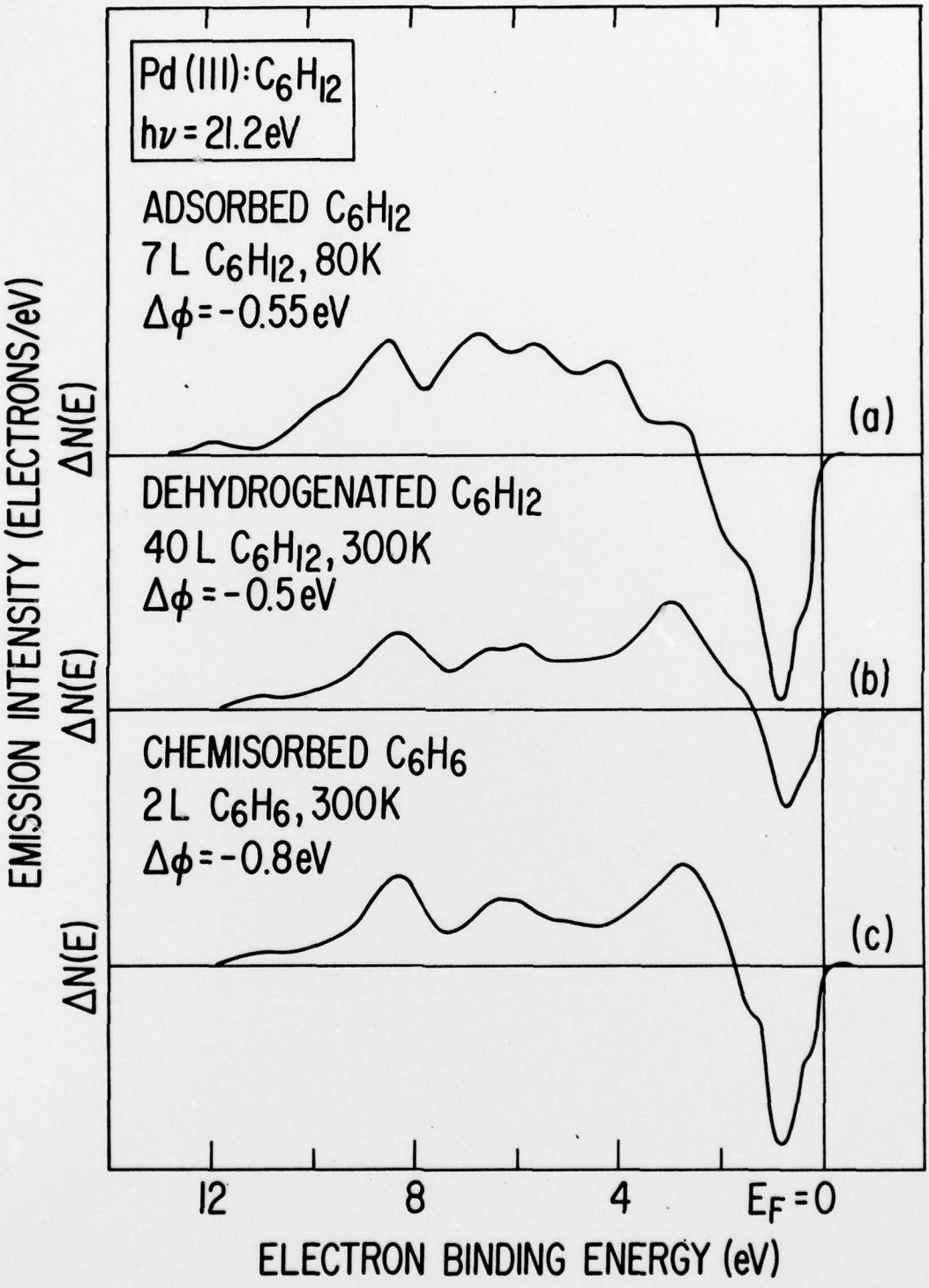
Pd (111): C_6H_{12}
$h\nu$ = 21.2eV
ADSORBED C_6H_{12}
7 L C_6H_{12}, 80K
$\Delta\phi$ = -0.55eV
(a)
DEHYDROGENATED C_6H_{12}
40 L C_6H_{12}, 300K
$\Delta\phi$ = -0.5eV
(b)
CHEMISORBED C_6H_6
2 L C_6H_6, 300K
$\Delta\phi$ = -0.8eV
(c)
EMISSION INTENSITY (ELECTRONS/eV)
ΔN(E)
ΔN(E)
ΔN(E)
12
8
4
E_F = 0
ELECTRON BINDING ENERGY (eV)

Fig. 3